LA-UR-01-1922
Approved for public release; distribution is unlimited.

Title:

Evaluating the hydrogeochemical response of springs using singular spectrum analysis and phase-plane plots

Author(s):

B.D. Newman, C.J. Duffy, and D.D. Hickmott

Submitted to:

http://lib-www.lanl.gov/la-pubs/00796103.pdf

Evaluating the hydrogeochemical response of springs using singular spectrum analysis and phase-plane plots

B.D. Newman
Earth and Environmental Science Div., Los Alamos National Laboratory, Los Alamos, NM, USA

C.J. Duffy
Civil and Environmental Engineering Dept., Pennsylvania State Univ., University Park, PA, USA

D.D. Hickmott
Earth and Environmental Science Div., Los Alamos National Laboratory, Los Alamos, NM, USA

ABSTRACT: An ongoing study is focused on understanding the hydrology and geochemistry of three contaminated, perennial, semi-arid zone springs at a high explosives production facility at Los Alamos National Laboratory, in northern New Mexico, USA. Springflow time series were examined using singular spectrum analysis (SSA) to identify the important time-scales affecting flow in the springs. SSA results suggest that springflow has two dominant patterns: a series of low-frequency modes which follow the seasonal and longer-term climate conditions at the site, and a large number of higher frequency modes which display the characteristic "red noise" spectrum related to local, short-term weather conditions. Phase–plane plots of $\delta^{18}O$ and spring discharge suggest that high flow conditions are dominated by snowmelt and summer monsoon inputs while low flow conditions can be affected by mixing of fast and slow flow components causing wide variations in $\delta^{18}O$ values. The analysis is being used for development of an efficient strategy for sampling design for environmental monitoring of contaminants that respond to multiple time scales.

1 INTRODUCTION

Since the 1950's, Los Alamos National Laboratory has carried out high explosives (HE) production on a semiarid zone mesa top location known as Technical Area 16 (TA-16, Figure 1). One of the consequences of the HE program has been the release of HE and other contaminants onto the mesa top and into adjacent canyons. As a result of these releases, the three perennial springs (SWSC, Burning Ground, and Martin springs) which flow along the TA-16 mesa sides have become contaminated, primarily with HE, barium, and nitrate. Currently, the TA-16 area is being investigated as part of the Los Alamos National Laboratory Environmental Restoration project (ER project), which includes characterizing the nature and extent of contamination at TA-16, installation of stabilization/best management practices, and source area removals. The three springs are a major focus of the environmental investigations because of the potential toxicity of the major contaminants from both an ecological and human health perspective and because the springs recharge alluvial systems in the canyon bottoms. There are two central issues regarding source removal effects and long-term monitoring that affect regulatory decision-making at the site. First, if source area removals are conducted on the mesa top, how long does it take before a reduction in contaminant concentrations are observed at a particular spring? Second, because a part of the

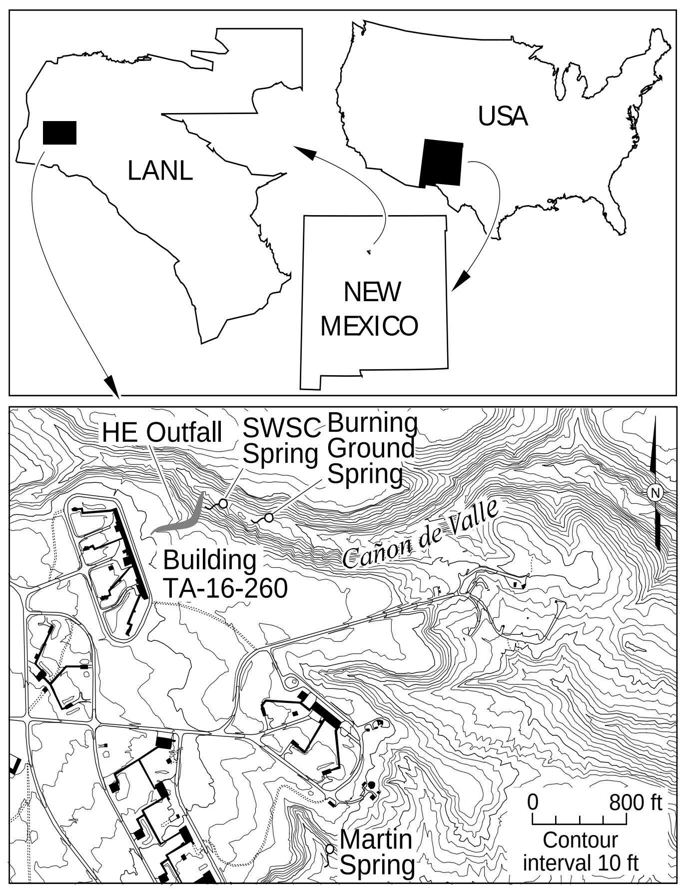

Figure 1. Location and contour map of TA-16 showing the location of HE production buildings; and Burning Ground, Martin, and SWSC springs.

contaminant inventory has moved from the original source areas into transient storage in the vadose zone where it cannot be realistically excavated, long-term monitoring of the springs will likely be required. This issue raises the question of what is the best sampling frequency to achieve the regulatory goals (which are yet to be determined) of long-term monitoring of the springs? High frequency (short time interval) sampling can achieve a high resolution of contaminant and flow variations with time. However, such a sampling strategy can be prohibitively expensive, especially for costly analytical suites such as HE. Alternatively, low frequency (long time interval) sampling might be economical, but may not capture the appropriate variations. These issues of understanding source removal effects and long term monitoring can only be adequately addressed by developing a representative conceptual hydrologic model of the site, and by understanding the characteristic times which control flow and transport in the springs. Here we present results based on interpretation of singular spectrum analysis of spring discharge and phase-plane plots of springflow and $\delta^{18}O$. The goal of the study is to improve the conceptual understanding of the spring flow systems and also provide a means for establishing long term monitoring strategies that are based on quantitative analysis of spring behavior.

2 METHODS

Daily spring flow has been measured at the three springs since 1996 using a v-notch weir with an automated data logger system. Stable isotope ($\delta^{18}O$) samples have been collected at the springs since 1999 using ISCO autosamplers programmed to collect samples on two-day intervals. A stable isotope precipitation collector was also installed on the mesa top in 1999, which consists of a large funnel and a "goose neck" tubing system (to prevent evaporation) connected to a 2-L storage bottle. Precipitation samples were collected on an event basis. All samples were stored in glass vials with polyseal caps. Additional sampling and analysis details and site description information can be found in Los Alamos (1998). Stable isotope analyses were conducted using standard isotope ratio mass spectroscopy methods at either the New Mexico Tech Stable Isotope Laboratory or GEOCHRON Laboratory. The CO_2 equilibration technique of Socki et al. (1992) was used for the $\delta^{18}O$ extractions. All $\delta^{18}O$ results are reported in permil based on the V-SMOW international standard.

Springflow time series were examined using Singular Spectrum Analysis (SSA), related to principal component analysis (see Elsner and Tsonis, 1996). SSA is used to determine the essential components of variability in a time series by decomposing the record into independent "modes". The objective is to capture the greatest amount of variability with the fewest modes. An important aspect of this data decompositon is that the resulting "modes" in the data can often be more easily interpreted or explained in terms of fundamental hydroclimatic regimes evident in the record. The details of SSA can be found in Elsner and Tsonis (1996). Shun and Duffy (1999) give an application to a hydrogeologic system. For this research, SSA was conducted using the springflow time series, and a set of MATLAB routines written to solve the SSA matrix and eigenvalue problems. Spectral analyses of time series are often conducted using Fourier-type approaches where the basis functions are sines and cosines. SSA differs from these other approaches in that the basis functions are data-adaptive, empirical, and orthogonal (Shun and Duffy, 1999). The advantage is that SSA captures the maximum variance with the fewest independent components, and as such, should lead to optimal, low-dimensional models. The objective of this SSA analysis is to estimate the periodic or nearly periodic oscillatory variance components in the flow time series which can then be related to hydroclimatic processes that control spring dynamics at TA-16.

Similar to autocorrelation analysis, SSA attempts to reveal underlying correlation structure from the lagged observations of a single time series. Letting $\boldsymbol{X}_{ij}$ be a matrix of time trajectories of the original time series, where i=1,2,3..,n rows of observations in time and j=1,2,3,….m columns represents the lagged series. The mxm correlation matrix

$$R = X^T X \tag{1}$$

is the sum of squares and products of lagged $\boldsymbol{X}$ where the data are standardized (mean removed and divide by standard deviation). The principal directions of R are found by solving the eigenvalue problem

$$(R - \lambda I)E = 0, \tag{2}$$

where λ are the eigenvalues, I is the identity matrix, and E are the eigenvectors. Note that the eigenvalues represent the variance contribution of each "component" in the series and the eigenvectors are the empirical basis functions. The method calculates the principal components of the series a by projecting the lagged series X onto the eigenvectors E. The k_{th} principal component is given by:

$$a_i^k = \sum_{j=1}^{m} x_{i+j-1} e_j^k \tag{3}$$

where i=1,2,….*n*, *j*=1,2,….*m*, and *e* is a matrix element. The time series can be recovered from the principal components by:

$$x_{i+j-1} = \sum_{k=1}^{m} a_i^k e_j^k . \tag{4}$$

One goal of SSA is to represent the original series *X* with fewer than "m" variance components.

In addition to SSA, phase-plane plots were constructed for the $\delta^{18}O$ versus discharge records. The trajectories of concentration-discharge plots are then used to make qualitative interpretations of the seasonality of the flow-transport relation for the spring and to examine the source and timing of recharge to the spring.

3 RESULTS & DISCUSSION

SSA was carried out on the three daily spring flow time series (Oct. 1996-May 2000). We will limit our discussion to the SWSC spring flow data as an example (Figure 2a). The SWSC time series is quite "noisy" in appearance, yet with SSA we were able to discern useful information about the timing of recharge and time scales controlling the flow variations.

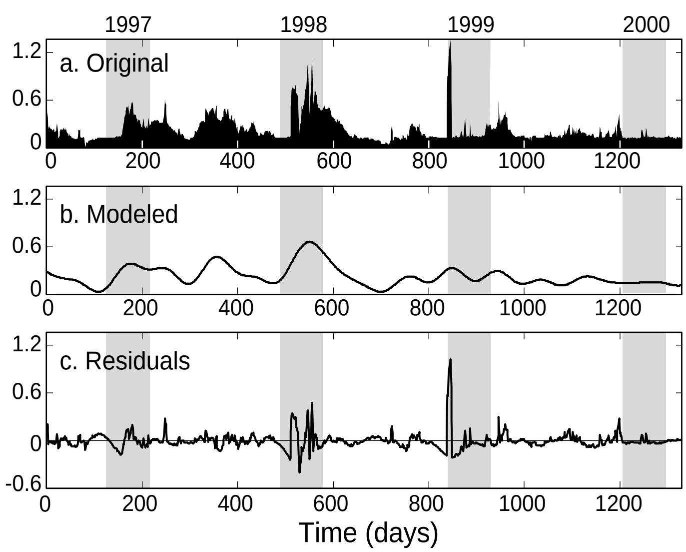

Figure 2. SWSC spring discharge ($m^3/s \times 10^{-3}$) (a), the reconstructed discharge ($m^3/s \times 10^{-3}$) using annual and seasonal low frequency modes (b), and model residuals that are related to the higher frequency modes (c). Note the weak snowmelt and weak monsoon in 1999-2000 that reduced spring discharge and represents a major factor in the 1999-00 drought. The shaded area represents the March-May spring melt period.

The eigenvalue spectrum for the SWSC spring is shown in Figure 3. In this case, the dominant modes are "low frequency" and represent the annual oscillation and its harmonics, the summer monsoon and the winter-spring snowmelt. From the confidence intervals on the spectrum, we also note that these are the only statistically significant modes or oscillations in the time series.

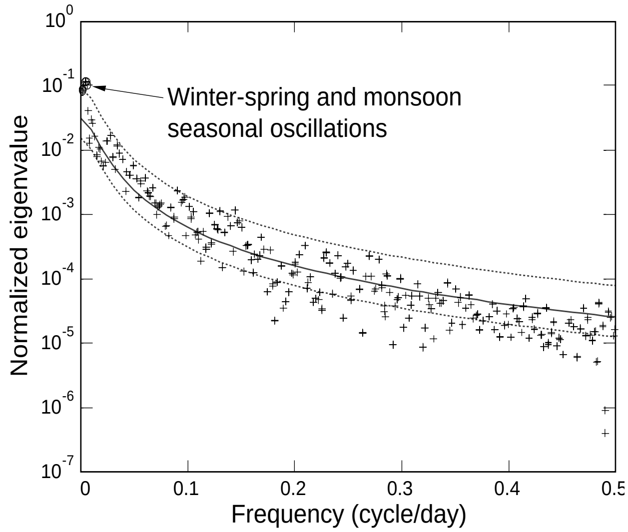

Figure 3. Eigenvalue spectrum of the SWSC springflow. The seasonal modes for the winter snowmelt and summer monsoon are indicated. The fitted line and 95% confidence interval represent a red noise spectrum.

The dominant modes are used to reconstruct the low-frequency part of the data with the "noise" removed (Figure 2b). The residual noise is shown in Figure 2c. The generally good agreement between the observed and modeled springflows (Figures 2a and 2b) illustrates that SWSC spring is dominated by the annual oscillation, which includes the winter-spring snowmelt and the summer monsoon. The shaded area on the plot indicates the March-May snowmelt period, and we note that the snowmelt response weakens significantly during 1999-2000. We also note that the monsoon is weak during this period. The springflow reconstruction clearly demonstrates the critical importance of both the monsoon and the snowmelt activity for initiating the drought conditions of 1999-2000. Overall, SWSC spring flow appears to be controlled by a few low frequency components (oscillations) with higher frequency noise components superimposed. In physical terms, the SSA results suggest that the spring is a low-pass system, with a characteristic relaxation time of a year or less that follows seasonal and longer-term climatic conditions. A second, high frequency response is related to local, short-term weather conditions at the site. The fast and slow time scales evident here are important to our conceptual model and will be examined further in the stable isotope discussion below.

Ideally, the singular spectrum results would be applied to the $\delta^{18}O$ time series as well. However, the stable isotope record was too short for this analysis. Another useful tool in the analysis of dynamical systems behavior is the phase-plane trajectory or concentration-discharge plot (Duffy and Cusumano, 1998). The $\delta^{18}O$ and discharge relation for SWSC spring is shown in Figure 4. Apparently, the low-flow $\delta^{18}O$ response of the spring varies over a wide range shifting from high to low values without a clear seasonal pattern. However, during high flow periods the $\delta^{18}O$ signal is quite clear. The monsoon $\delta^{18}O$ value is in the range of -9 to -10‰, while the snowmelt response is in the range of –10.5 to –12‰, and both are consistent with measured $\delta^{18}O$ values in precipitation and snowmelt during the monsoon and spring seasons. Note that during the study period, the monsoon response for 1998 and 1999 did not develop in the springflow record (Figure 2a) reflecting the drought conditions for those years.

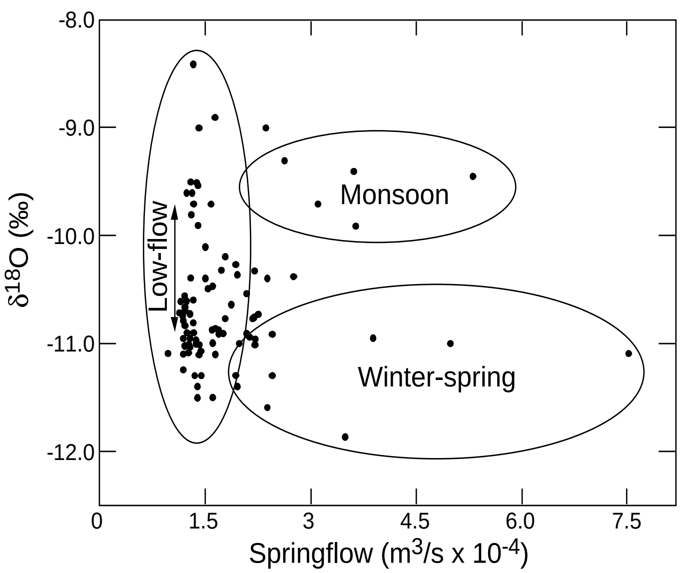

Figure 4. The $\delta^{18}O$-springflow phase-plane response for SWSC spring suggesting seasonal mixing of low-flow $\delta^{18}O$ and the characteristic response of the monsoon and snowmelt $\delta^{18}O$-springflow relationship during high flow.

As the $\delta^{18}O$ time series gets longer at the site we expect to begin to unravel the low-flow response as well, but at this time, it appears that the relaxation time of the spring is probably not greater than a year. If it were larger, the seasonal shift in $\delta^{18}O$ would not be so distinct and a mixed response would be evident. In fact, Burning Ground spring (data not shown) apparently has a somewhat larger residence time since the phase-plane plots in that case show a mixed response during high flow periods.

The $\delta^{18}O$ data from the springs exhibits a relatively short relaxation time in another way. During the 2000 drought, the variability of $\delta^{18}O$ in the spring waters was greatly reduced, and spring temperature data show the same effect. This reduction in variability probably resulted from the large decrease in recharge from the fast, normally high frequency recharge pathways that were essentially shut down during the drought. Thus, the isotopic compositions of the springs during the drought period should largely reflect that of the longer residence time, perennial part of the flow system that is affected by the low frequency oscillations. By using the $\delta^{18}O$ values from the drought period, we can estimate the elevation of recharge for the perennial part of the flow system and see if the distance between the recharge area and the springs is consistent with a short relaxation time.

Vuataz and Goff (1986) established the following relation between elevation and isotopic composition:

$$\text{Elevation (m)} = -314(\delta^{18}O)-1161 \qquad (5)$$

Using the smallest isotopic value (-11.3‰ at Burning Ground spring) measured during the drought to estimate the “maximum” recharge elevation from equation 1, results in an estimate of 2387 m for the recharge elevation. This estimate suggests that spring recharge occurs less than 2 km west of the springs. This location is coincident with a known fault zone associated with the Jemez Mountains. Other $\delta^{18}O$ values measured during the drought period yield even lower elevation estimates. Thus, the relatively small distances between recharge zones and the springs are consistent with short relaxation times.

In terms of developing a long-term, contaminant monitoring program for the springs, we do not currently have sufficient data to make a reliable sampling design. However, the SWSC flow results discussed above provide a good example of how SSA can be used to design such a strategy. The SSA results (Figure 2), suggest that sampling should be frequent enough to capture the quarterly and longer time-scale oscillations. In order to capture a particular oscillatory behavior, a minimum sampling frequency of one half of the cycle time is required, for example, 45 days for the quarterly (90 day) oscillation. However, one half the cycle time is a minimum sampling frequency and for the quarterly oscillation, a monthly sampling is better and can account for any phase shift variations. In other words, a monthly strategy would be adequate to capture at least 40% of the total variance in spring flow. In addition, to capture rapid responses to high-frequency stochastic events, we would propose a threshold-based sampling triggered for example, on a specified rate or volume of precipitation.

4 SUMMARY AND CONCLUSIONS

The analyses presented here will aid in understanding time scales of contaminant transport to the springs and provide support for development of a long-term monitoring program. Without a quantitative approach to sampling frequency, long-term monitoring will not be based on actual spring dynamics. By having a quantitative method to evaluate sampling frequency we also hope to avoid adversarial situations that pit regulators who desire a high frequency sampling rate, against site owners who desire an affordable, easily implementable rate. Future work at the site involves collection of additional flow and stable isotope data, which will lead to a more complete set of SSA analyses and allow a more robust concentration-discharge relationship. In terms of model development resulting from this analysis, we hypothesize that the "fast flow" component is modulated by the slower annual oscillations. This suggests a threshold-type recharge response where a large moisture deficit must be satisfied before recharge to the springs can occur.

5 ACKNOWLEDGEMENTS

We would like to thank the Los Alamos Environmental Restoration Program and the Los Alamos CULAR program for supporting this research effort. Contributions by Deb Bergfeld, Peter Gram, Randy Johnson, Lynn Kidman, Andi Kron, Eli Ludwig, and Donna Sharp are appreciated. The second author acknowledges the support of the NSF Science & Technology Center SAHRA (EAR-9876800) for the final stages of this work.

REFERENCES

Duffy, C.J. and J. Cusumano, 1998, On the Validity of Low-Dimensional Models for Concentration-Discharge Dynamics in Stream-Aquifer Systems, *Water Resources Research*, 34(9), 2235-2247.

Elsner, J. B. and A. A. Tsonis. 1996. Singular Spectrum Analysis. Plenum Press, NY. 164 pp.

Los Alamos National Laboratory. 1998. RFI report for pontential release site 16-021(c). Los Alamos National Laboratory Report, LA-UR-98-4101

Shun, T. and C. J. Duffy. 1999. Low-frequency oscillations in precipitation, temperature, and runoff on a west facing mountain front: A hydrogeologic interpretation. Water Res. Research, 35:191-201.

Socki, R. A., H. R. Karlsson, and E. K. Gibson. 1992. Extraction technique for the determination of oxygen-18 in water using preevacuated glass vials. Anal. Chem., 64, 829-831.

Vuataz, F.-D. and Goff, F. 1986. Isotope chemistry of thermal and nonthermal waters in the Valles Caldera, Jemez Mountains, Northern New Mexico. J. Geophys. Res., 91(B2) , 1835-1853.